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A METHOD FOR PREPARING A COMMERCIAL GRADE OF CALCIUM ARSENATE.

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CALCIUM ARSENATE AS A SUBSTITUTE FOR LEAD ARSENATE.

Attention has been directed to the use of calcium arsenate as a substitute for lead arsenate, principally because of the cheapness of lime as compared with the cost of lead oxid. While no one recommends the use of calcium arsenate alone on tender foliage, experiments by investigators in the United States Department of Agriculture [1] and in the Canadian Department of Agriculture [2] and others have shown that it gives excellent results on some of the more resistant plants, as well as very promising results when combined with other sprays, especially sulphids, which cause to some extent the breaking up of lead arsenate. The greatest development in its use, however, has been for the control of the cotton boll weevil, many million pounds being used each year for this purpose.

PREPARATION OF CALCIUM ARSENATE.

The Bureau of Entomology of this department has conducted experiments with "homemade" calcium arsenate prepared by slaking burned lime with a solution of sodium arsenate. Others [3] have

[1] U. S. Dept. Agr. Bul. 278: Farmers' Bul. 908.
[2] Crop Protection Leaflet 10.
[3] Oregon Agr. Exp. Sta. Bul. 131.

recommended calcium arsenate prepared by the action of soluble lime salts on sodium arsenate. In all such cases soluble by-products are formed. Since these may influence the action of the spray, they should be washed and filtered out if a good grade of commercial calcium arsenate is desired.

From the chemical standpoint, the simplest means of producing calcium arsenate is the direct union of calcium hydroxid and arsenic acid. As the sole by-product of this reaction is water, filtration of the material is the only treatment that should be required, thus eliminating the washing necessary with most products.

The experiments here reported were made with the idea of determining the proportions and procedure necessary to obtain a product having the properties desired for spraying purposes.[4] The arsenic acid used was commercial 75 per cent acid, with a density of 1.88, corresponding to 61 per cent arsenic oxid (As_2O_5), or 75 per cent arsenic acid (H_3AsO_4). The lime was a good grade of commercial lime of the following composition:

	Per cent.
Loss on ignition	5.07
Calcium oxid (CaO)	93.36
Magnesium oxid (MgO)	.69
Silicon dioxid (SiO_2)	.54
Oxids of iron and aluminum (R_2O_3)	.68
	100.34

The most desirable method of uniting lime and arsenic acid is to have both ingredients in solution before they are mixed. This necessitates the use of limewater which contains only about 1 gram of calcium oxid per liter, and of a quantity of water so large that it probably would be prohibitive in commercial practice. Nevertheless, a few experiments were made to discover the nature of the product so formed.

If arsenic acid of any strength is added slowly to limewater containing phenolphthalein until the latter is just about to decolorize, a gelatinous, slow-settling precipitate is formed. After the lapse of an hour or so, this crystallizes and settles to about one-eighth of the volume of the liquid used. The precipitate filters very readily, leaving a cake which on the steam bath dries fairly rapidly to very light lumps easily powdered between the fingers. Its extreme lightness is noticeable, and it does not require grinding, simply a disinte-

[4] The desirable features of a good arsenical spray material are as follows: It should not contain an excessive quantity of soluble arsenic, which would cause injury to foliage; it should be very finely divided so that it may be distributed well over the foliage; it should be light when in the dry form, to permit of ready application by dusting; it should suspend well in water, to permit of even distribution when applied in the form of a spray; and when sprayed and subsequently dried it should stick well to the foliage.

gration of the lumps. One preparation, dried at about 70° C. on the steam bath, had the following composition:

	Per cent.
Calcium oxid (CaO)	32.00
Arsenic oxid (As_2O_5)	42.96
Water (by difference) (small quantity of CO_2)	25.04
	100.00

The molecular ratio of CaO to As_2O_5 is here 3.05 to 1, showing the compound to be tricalcium arsenate. Its formula approximates most closely to $Ca_3(AsO_4)_2.8H_2O$, a compound which has been shown to exist by the Department of Agriculture. Drying at 110° C. results in the loss of about seven of the eight molecules of water of crystallization. The lightness of this material may be judged from the fact that 2 ounces of it filled a graduated cylinder to the 500 cubic centimeter mark, which is equivalent to 240 cubic inches per pound, this, of course, without any attempt at packing. If jarred for a sufficient time the space occupied will be reduced to about 60 per cent of this figure.

The compound thus formed yields appreciable quantities of soluble arsenic when treated with water. In one experiment 1.8 grams was treated with 1 liter of water (equivalent in arsenic content to 1 pound of dilead arsenate in 50 gallons) for 24 hours, and 55 milligrams, or 3.04 per cent, of arsenic oxid was rendered soluble. R. H. Robinson[5] found 79 milligrams of arsenic oxid per liter for somewhat similar material. This, of course, is excessive, and would make the material unfit for use alone on any but the hardiest foliage, such as will stand applications of Paris green.

If the manufacture of calcium arsenate by this process were attempted commercially, the liquid left from the settling of one batch of arsenate could be used again for the preparation of more lime-water, and thus the consumption of water might be greatly reduced. However, methods requiring the handling of as little material as possible probably would be preferable. On first thought, such a process would be the direct slaking of the stone lime with an arsenic acid solution of the requisite strength. But such a procedure is not practicable. Owing to the slow surface action, the arsenic oxid is locally always in excess, resulting in the formation of dicalcium or even monocalcium arsenate (if the arsenic acid is strong enough), which, while it may be changed later by the excess of lime, renders the product lumpy or granular. Even the use of strong arsenic acid with a concentrated lime paste suffers from the same drawbacks. The addition of the acid causes a further thickening of the paste, and thorough and rapid mixing becomes impossible.

[5] Oregon Agr. Exp. Sta. Bul. 131, p. 7.

SLAKING THE LIME.

Only dilute lime paste, made by slaking quicklime, was used in the experiments here reported. It is self-evident that the ease with which such a paste will combine with acid is directly dependent on the smoothness of the paste. Consequently, experiments to determine the best procedure to follow in slaking, so that the paste would be smooth and free from lumps, were made first.

The use of 3 to 3½ times as much water (by weight) as lime gave a paste which was entirely satisfactory, if the lime employed was sufficiently pure. This produced a paste rather thick, but not thick enough to interfere with good mixing when working with small quantities. Best results were obtained by using boiling water for slaking, although in bulk the natural heat of reaction would be sufficient.

PROPORTIONS OF ARSENIC OXID AND LIME.

For spraying purposes a compound must be free, or nearly so, from arsenic in water-soluble forms. Practically pure crystalline tricalcium arsenate is appreciably affected by water. All of the calcium arsenates more acid than this are likewise somewhat soluble (or decomposable), the action increasing until the monoarsenate, which is readily soluble in water, is reached. Evidently, then, it is necessary to look toward the basic side.

It has long been known that the addition of an excess of lime to a spraying compound makes the arsenic insoluble. The object here was to find the right proportions to produce a material combining high arsenic oxid content with sufficiently low water-soluble arsenic oxid to prevent burning or reduce it to the lowest possible limit. Two series of experiments were made along this line. Each series included eight experiments, the molecular ratio, CaO to As_2O_5, being varied from 3 to 5 by appropriate steps. The quantity of arsenic oxid used was kept constant, being 25 cubic centimeters of a solution containing 0.4 gram of arsenic oxid per cubic centimeter (in other words, a total of 10 grams of arsenic). The weighed quantities of lime were slaked in beakers with three times their weight of boiling water, and the cold arsenic solution was added slowly, from a pipette, with constant stirring. In one series (*A*) the acid was added to the lime while still hot from slaking; in the other series (*B*) the lime paste was permitted to cool to room temperature before mixing. Each mixture was then divided into two portions. One portion was permitted to stand over night and was then decanted. The other was filtered and sucked as dry as possible on a Büchner funnel. Water was determined in portions of each paste by drying in the oven at 105° C. The dried portions were used for chemical analysis. The water-soluble arsenic was determined on the dry material, using 1.2 grams in 500 cubic centimeters (equivalent to 1 pound in 50 gallons). The results of these experiments are summarized in Table 1.

TABLE 1.—*Analysis of experimental preparations.*

Designation.		Lime used.	Arsenic oxid used.	Water in—		Analysis of material dried at 105° C.		Molecular ratio, CaO/As_2O_5.	Soluble arsenic (As_2O_5).	Dried material per pound.
Exp. No.	Series No.			Settled material.	Filtered material.	CaO.	As_2O_5.			
		Grams.	*Grams.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*		*Per cent.*	*Cubic inches.*
1	*A*	7.30	10	52.5	36.2	35.52	52.71	2.76	11.51	60
	B	7.30	10	66.1	58.8	37.30	51.76	2.95	8.26	82
2	*A*	7.79	10	59.2	47.7	38.75	51.84	3.07	5.06	66
	B	7.79	10	67.5	59.2	38.70	51.53	3.08	4.52	77
3	*A*	8.28	10	61.7	51.2	39.70	50.77	3.20	2.51	68
	B	8.28	10	67.8	53.8	40.59	50.17	3.17	1.52	76
4	*A*	8.77	10	64.6	51.1	41.15	49.46	3.41	1.83	68
	B	8.77	10	66.8	53.9	41.49	48.00	3.54	1.14	80
5	*A*	9.25	10	59.8	50.4	40.45	46.38	3.58	.48	60
	B	9.25	10	67.7	54.3	42.32	46.22	3.75	.42	76
6	*A*	9.74	10	59.2	52.4	42.02	46.17	3.73	.50	62
	B	9.74	10	66.9	51.5	42.90	43.22	4.07	.19	72
7	*A*	10.96	10	60.7	48.5	43.67	41.42	4.32	.25	70
	B	10.96	10	66.7	49.6	44.80	43.36	4.24	.06	80
8	*A*	12.17	10	67.7	54.2	45.76	39.26	4.78	.27	74
	B	12.17	10	66.1	58.0	47.06	40.32	4.79	(1)	83

[1] Lost.

In every case Series *B* gave lower soluble arsenic figures than Series *A*. Only when the ratio CaO to As_2O_5 is 4 or more does the soluble arsenic decrease to about 0.2 per cent. All commercial calcium arsenates therefore should be at least as basic as $4CaO.As_2O_5$, upon which ratio all later experiments were based. The content of water of constitution, and that probably of crystallization (about 14 per cent), might be reduced by heating to a sufficiently high temperature if this proved desirable from a commercial standpoint.

Probably next in importance to the question of soluble arsenic comes the question of lightness of material, that quality which governs suspension in water. This is controlled by two things, actual density and size of particles. All the calcium arsenates have densities around 3, approximately half that of the corresponding lead compounds. This is a characteristic property of each compound, practically independent of conditions. The size of particles, however, is influenced by the manner of mixing, the temperature, the concentration, etc. In the experiments reported in Table 1, the arsenic acid was added slowly to the lime in the belief that it was best to prevent even the slightest local excess of acid. It was found later, however, that rapid mixing gave a product which was much more easily powdered.

Table 1 also shows that temperature has a marked effect, a more bulky product being formed when the solutions are mixed in the cold.

EFFECT OF DILUTION AND TEMPERATURE UPON THE COMPOUND.

A group of 16 experiments was designed to show the effect of dilution and temperature upon "lightness." In all the experiments the quantity of lime and acid used was the same—11 grams of lime (93 per cent calcium oxid) and 10 grams of arsenic oxid. In every case the lime was slaked with 35 cubic centimeters of boiling water. Four temperature combinations were used: Both hot; lime hot, acid cold; acid hot, lime cold; both cold. Four dilutions were used. In every case the acid was dumped as quickly as possible into the lime.

In the more concentrated mixtures, especially when warm, reaction took place rapidly, phenolphthalein being reddened immediately. But as the dilution increased and the temperature fell, action was delayed, the solution remaining acid for perhaps 10 minutes. No doubt this is due to the fact that the acid does not penetrate instantaneously into the small particles of lime in suspension. When both solutions are hot the reaction is violent, causing rapid boiling, while when both solutions are cold, only a moderate rise in temperature occurs. For instance, the temperature rose from 32° C. to 65° C. in 4 *A*, and from 32° C. to 40° C. in 4 *D*.

After being mixed and standing for 15 to 20 minutes, the precipitates were filtered off and dried overnight on the steam bath. Portions were then sieved through a No. 100-mesh sieve, and their bulkiness was compared by measuring the volume occupied by 2.77 grams in a 10-cubic centimeter graduated cylinder. Ten times the figure read on the cylinder is equivalent to the number of cubic inches per pound. The measurements were taken just as the material was poured into the cylinders, no attempt being made to pack it. Entomologists have stated that a good calcium arsenate for dusting purposes should occupy from 70 to 90 cubic inches per pound. Such determinations, however, are comparable only when conducted in the same way.

The results of these experiments are summarized in Table 2.

TABLE 2.—*Effect of dilution and temperature on lightness of spraying compounds.*

Experiment No.	Temperature.	Degree of dilution and lightness of compound.			
		A	*B*	*C*	*D*
		11 gm. lime—35 cc. H_2O. 10 gm. As_2O_5—25 cc. H_2O.	11 gm. lime—70 cc. H_2O. 10 gm. As_2O_5—50 cc. H_2O.	11 gm. lime—105 cc. H_2O. 10 gm. As_2O_5—75 cc. H_2O.	11 gm. lime—140 cc. H_2O. 10 gm. As_2O_5—100 cc. H_2O.
1	Lime hot, acid cold	*Cu. in. per lb.* 60	*Cu. in. per lb.* 96	*Cu. in. per lb.* 104	*Cu. in. per lb.* 128
2	Acid hot, lime cold	60	104	126	112
3	Lime hot, acid hot	60	78	92	98
4	Lime cold, acid cold	86	104	90	80

The general tendency is toward a production of lighter material in lower concentrations. But here a new feature, the hardness of the lumps and the effort necessary to reduce them to powder, makes its appearance. Amorphousness is usually associated with the production of hard, lumpy residues on drying, as, for example, in the case of aluminum hydroxid. So here 1 *D*, 2 *C*, and 2 *D*, the lightest of the powders, produce hard lumps, 2 *D* being the hardest of the lot. It was difficult to break them in the fingers, and for commercial use they would almost certainly have to be ground. On the other hand, 4 *A* and 4 *D* were crumbly, and could be readily reduced to powder by shaking. Probably, then, a compromise between a method of preparation which produces the lightest powder and a method which produces the most easily pulverized powder would be necessary.

Equal bulkiness is shown for 2 *B*, 4 *B*, and 1 *C*, all of which, especially 1 *C*, were easily powdered. *Based on this work, the authors believe that the most advantageous method to produce a reasonably light*

material, which at the same time is easily pulverized, is to slake the lime, add two more volumes of hot water, and then add the cold arsenic acid solution as rapidly as possible (method 1 *C*). Methods 4 *B*, 2 *B*, and 4 *A* also, however, give a product which is reasonably light and easily pulverized.

None of these products, except the tricalcium arsenate mentioned on page 3, is as bulky as some of the commercial dilead arsenates which run as high as 140 cubic inches per pound when measured in the manner prescribed here. This calcium arsenate, however, yields an excessive quantity of water-soluble arsenic, and is prepared by a method that is hardly practicable under manufacturing conditions.

EXPERIMENTS WITH LIMESTONE.

It was at first thought that calcium arsenate might be made directly from limestone, instead of from lime, thus saving the expense of burning. A few experiments showed that calcium carbonate reacts readily with arsenic acid at room temperature, and continues to do so until the solution is about neutral to methyl orange. At this point the solution contains calcium oxid and arsenic oxid in the proportions to form calcium monoarsenate ($CaH_4(AsO_4)_2$). If this solution is heated by itself, it deposits crystals of dicalcium arsenate ($CaHAsO_4.H_2O$), which on continued boiling lose their water of crystallization ($CaHAsO_4$). In the presence of excess calcium carbonate, reaction continues until practically all the arsenic oxid has been precipitated as $CaHAsO_4$. This, however, takes place readily only if the carbonate is in a fine state of division, and hardly at all if it is in pea-sized lumps. Calcium carbonate is not alkaline enough to carry the conversion to the tricalcium arsenate stage. This dicalcium arsenate is fairly crystalline and granular, and, owing to its solubility and other physical properties, is not well suited for use as a spray. It could, of course, be mixed with excess lime, but, because of its granular nature, reaction would be slow, and when sprayed the lime might be completely carbonated before some of the crystals were changed, thus giving a chance for injury by the soluble arsenic. All things considered, it appears that there is no advantage in attempting to substitute limestone for lime.

SUMMARY.

The most desirable procedure for making calcium arsenate from lime and arsenic is as follows:

1. Use a good grade of lime, containing a high percentage of calcium oxid.

2. Slake the lime to as smooth a paste as possible, for upon this depends the smoothness of the final product, as well as the readiness with which the lime and acid react. Use from 3 to 3½ times as

much water, by weight, as lime, and have it, preferably, warm. Let it stand for a while and then thoroughly mix, after which add twice as much hot water as was used for slaking, and mix again.

3. The lime and arsenic should be in such proportion that the weight of actual calcium oxid used will equal that of the arsenic oxid used. This gives a product with a molecular ratio slightly over 4 to 1, which is necessary if the soluble arsenic oxid is to be kept down to desirable limits.

4. Add the acid at room temperature to the lime as quickly as possible and stir well until the liquid becomes alkaline to phenolphthalein.

5. Filter to as dry a state as possible. Do not wash. If a dry product is desired, dry directly in any suitable manner.

6. Crush in a suitable disintegrator, or grind if necessary.

The production of 100 pounds of a commercial grade of calcium arsenate by this process will require 45 pounds of calcium oxid (approximately 50 pounds of a high-grade lime) slaked with 18 gallons of water, the addition of 36 gallons of water, and then of 45 gallons of a solution containing 1 pound of arsenic oxid per gallon. A slight departure from the quantities given for water will probably have little effect.

LABELING THE PRODUCT.

A product prepared in accordance with the procedure outlined is, of course, not pure calcium arsenate, but consists of tricalcium arsenate, probably with some water of crystallization, together with excess of other calcium compounds, such as calcium hydroxid and calcium carbonate. The product, therefore, should not be designated simply "Calcium Arsenate," but by some such term as, "Calcium Arsenate Containing other Calcium Compounds." In labeling such a product, the following is suggested by the Insecticide and Fungicide Board of this department as the simplest form of statement which will fulfill the requirements of section 8 of the insecticide act of 1910, relating to the statement of active and inert ingredients and total and water-soluble arsenic.

Active ingredient:
Tricalcium arsenate..... ——%
Inert ingredients..... ——%
Total arsenic (as metallic)..... ——%
Arsenic in water-soluble forms (as metallic)..... ——%

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